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III.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON THE CUPRIAMMONIUM DOUBLE SALTS.

THIRD PAPER.

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THE work already done upon the double salts of cupriammonium* suggested the possibility of obtaining compounds of fluorine and iodine similar to those of chlorine and bromine.

Many attempts were made to prepare cupriammonium acetofluoride, $\text{Cu}(\text{NH}_3)_2\text{FC}_2\text{H}_3\text{O}_2$, with invariable failure. The methods and the proportions of the reagents were varied in every possible way; but nothing could be obtained beside cupriammonium acetate and ammonium fluoride. Cupriammonium fluoride itself is very difficult to prepare, because of its solubility; and it is not unnatural that the double salt should be more so. It will be remembered, moreover, that while cupriammonium acetobromide is very easy to obtain, the normal chloride is almost if not quite impossible by the wet way. We should expect the fluorine compound to be even less possible. Because of these continued failures, the work with fluorine was discontinued.

The investigation of the compounds of iodine proved much more fruitful, yielding the following new substances:—

- (1.) $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$.
- (2.) $7 \text{ Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}(\text{NH}_3)_2\text{IC}_2\text{H}_3\text{O}_2$.
- (3.) $3 \text{ Cu}(\text{NH}_3)_2 \cdot \text{I}_2 \cdot 4 \text{ NH}_3$.
- (4.) $2 \text{ Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$, besides confirming the work of Foerster † on the following substances:—
- (5) $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2$.
- (6) $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2 2\frac{1}{2}\text{H}_2\text{O}$.

* Richards and Shaw, These Proceedings, XXVIII. 247; Richards and Whitridge, These Proceedings, XXX. 458.

† Berichte der deutsch. chem. Gesellsch., XXV. 3416.

(1.) AMMON-CUPRIAMMONIUM ACETO-IODIDE,
 $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_8\text{O}_2$.

In preliminary experiments the following method was used for preparing this compound. Four grams of finely powdered cupric acetate were stirred with a mixture of ten cubic centimeters of water, twenty of alcohol, and eight of glacial acetic acid. Ammonia gas was then passed into the mixture until all the cupric acetate was dissolved and the color of the solution had become deep blue. After the addition of three and a half grams of ammonic iodide the solution was set aside to crystallize, and in about six hours large deep blue monoclinic plates, having a six-sided outline, separated out. These crystals were washed with alcohol, and then dried between filter papers as quickly as possible. The salt thus prepared is usually not very pure, hence subsequently more alcohol was used in the preparation, with better success. Even yet, however, there was much room for improvement.

After many systematic experiments, which need not be detailed, the following method was found to yield very excellent results. Twelve grams of cupric acetate were dissolved in fifty cubic centimeters of ammonia water (sp. gr. = 0.90) in a flask. After cooling, thirty cubic centimeters of aqueous acetic acid (57 per cent) were added to the solution, then six grams of ammonic iodide, and finally fifty cubic centimeters of alcohol. Upon boiling over the water bath the mixture yielded a clear deep blue solution, which deposited crystals of ammonium-cupriammonium aceto-iodide upon slow evaporation in the air. The first very small crop of crystals deposited upon cooling was not analyzed. The second served for Analysis IV. below, and the third crop, which was altogether the purest and best defined in crystalline form, served for Analyses V. and VIII. The substance used in Analyses I., II., III., VI., and VII. was prepared by earlier less satisfactory methods; it was undoubtedly the same substance, however.

Ammon-cupriammonium aceto-iodide consists of brilliant deep blue monoclinic crystals. It is not very permanent in the air, although much more so than its chlorine and bromine analogues. Upon exposure for a long time the crystals become dull and dark in color, and the substance slowly loses in weight. Water at once decomposes it, some of the copper going into solution, and the rest remaining as a basic precipitate. Acids set free iodine and precipitate cuprous iodide, as might be expected. The only unexpected property of the salt is the fact that it contains no crystal water, thus not maintaining a strict analogy with the corresponding chlorine and bromine compounds.

$\text{Cu}(\text{NH}_3)_3\text{ClC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$. The reason for this anomaly remains obscure.

The ammonia present in the compound was determined by distillation with pure potash or soda, the distillate being titrated with standard acid. It is convenient to prepare the alkali for this purpose directly from metallic sodium or from sodium amalgam, thus avoiding the complications in the subsequent proceedings introduced by the usual impurity of chlorine in commercial potash and soda. The residue in the distilling flask after the ammonia had been expelled was filtered, and to the filtrate was added a little sulphurous acid to reduce any iodate which might have been formed. Argentic nitrate was then added, and subsequently the argentic oxide and sulphite were dissolved by nitric acid, the argentic iodide being collected and weighed upon a Gooch crucible. In Analysis IV. the alkali was nearly neutralized, and in Analysis V. the solution was just acidified by pure nitric acid before the precipitation. In every case enough nitric acid was added after the precipitation to insure the solution of all but argentic iodide, and the agreement of the results is sufficiently satisfactory. The copper was determined by the electrolysis of the cupric sulphate obtained from the precipitated cupric oxide, which contained no trace of iodine; and the acetic acid was determined by combustion.

Analyses of $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$.

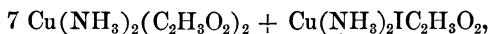
- I. 0.2591 gram of the substance on distillation with potash required 25.34 cubic centimeters of decinormal acid for neutralization, gave on electrolysis 0.0545 gram of copper, and yielded 0.2042 gram of argentic iodide.
- II. 0.2524 gram of the substance required 25.05 cubic centimeters of decinormal acid and gave 0.0527 gram of copper.
- III. 0.2322 gram of the substance required 23.25 cubic centimeters of decinormal acid.
- IV. 0.3960 gram of the substance gave 0.3109 gram of argentic iodide.
- V. 0.2559 gram of the substance gave 0.2004 gram of argentic iodide.
- (VI.) 0.3211 gram of the substance gave on combustion 0.0939 gram of carbon dioxide.
- VII. 0.2946 gram of the substance gave on combustion 0.0864 gram of carbon dioxide.
- VIII. 0.3062 gram of the substance gave on combustion 0.0907 gram of carbon dioxide.

No.	Copper.	Ammonia.	Iodine.	Acetic Acid.
I. . . .	21.03	16.73	42.58	
II. . . .	20.88	16.95		
III. . . .	—	17.10		
IV. . . .	—	—	42.41	
V. . . .	—	—	42.31	
VI. . . .	—	—	—	19.62
VII. . . .	—	—	—	19.64
VIII. . . .	—	—	—	19.86
Averages .	20.96	16.99	42.43	19.71

	Calculated for $\text{Cu}(\text{NH}_3)_8\text{IC}_2\text{H}_8\text{O}_2$	Found.
Copper	21.15	20.96
Ammonia	17.03	16.99
Iodine	42.19	42.43
Acetic acid	19.63	19.71
	100.00	100.09

(2.) OCTOCUPRIAMMONIUM MONO-IODIDE ACETATE,
 $\text{Cu}_8(\text{NH}_3)_{16}\text{I}(\text{C}_2\text{H}_8\text{O}_2)_{15}$.

On allowing the mother liquor left over from the first method of preparing ammon-cupriammonium aceto-iodide to stand for a long time, large coal-black hexagonal crystals of unknown composition were deposited. Mixed with these were large blue crystals, which were separated mechanically from the black ones, and analyzed. The analysis corresponded closely with the formula



the complexity of which led to the suspicion that the crystals were a mixture instead of a definite compound. Nevertheless, upon qualitative testing, the smallest as well as the largest crystals were found to contain iodine.

In external appearance the crystals, which were usually at least half a centimeter in length, resembled those of cupriammonium acetate. An attempt was made to measure the angles of the crystals of each

substance, but the faces were so covered with striations that the result was only partially satisfactory. For cupriammonium acetate the chief prism angle was about 70° , while for the complicated salt under consideration it was over $71^\circ 30'$. Even allowing a considerable margin for possible error, it would appear that the complicated salt must be a definite compound, and not merely cupriammonium acetate containing occluded cupric acetate and ammonic iodide. Another evidence of the probable definiteness of the salt is to be found in the fact that Richards and Moulton, in a paper yet to be published, have proof of the existence of a similar compound containing aniline and bromine instead of ammonia and iodine. The compound has no unexpected properties, and was analyzed in the usual fashion.

Analysis of $\text{Cu}_8(\text{NH}_3)_{16}\text{I}(\text{C}_2\text{H}_8\text{O}_2)_{15}$.

- I. 0.2545 gram of the substance distilled with potash required 22.68 cubic centimeters of decinormal acid, gave 0.0333 gram of argentic iodide, and on electrolysis yielded 0.0707 gram of copper.
- II. 0.2120 gram of the substance required 18.52 cubic centimeters of decinormal acid.
- III. 0.2419 gram of another sample of the substance required 21.23 cubic centimeters of acid, and gave 0.0331 gram of argentic iodide and 0.0680 gram of copper.

No.	Copper.	Ammonia.	Iodine.
I.	27.78	15.25	7.07
II.	—	14.93	
III.	28.11	14.99	7.39
Averages . .	27.95	15.05	7.23

	Calculated for above Formula.	Found.
Copper	28.35	27.95
Ammonia	15.22	15.05
Iodine	7.07	7.23
Acetic acid (by dif.)	49.36	49.77
	100.00	100.00

Every effort to make the normal cupriammonium aceto-iodide free from the acetate was unsuccessful; when so much of the ammonia has evaporated that $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$ ceases to form, the singular double salt which has just been described always makes its appearance.

(3.) TETRAMMON-TRICUPRIAMMONIUM IODIDE,
 $3 \text{Cu}(\text{NH}_3)_2\text{I}_2 + 4 \text{NH}_3 = \text{Cu}_8\text{I}_6(\text{NH}_3)_{10}.$

This interesting substance may be prepared by a method very closely resembling that used for preparing ammonium-cupriammonium aceto-iodide. If eight grams instead of twelve of cupric acetate are used with fifty cubic centimeters each of ammonia and alcohol, thirty of acetic acid, and six grams of ammonic iodide, curious black crystals resembling irregular triangular pyramids make their appearance in the first place.

The new substance is similar in outward aspect to the corresponding bromine compound,* although less brilliant. The crystalline faces are so singularly marked and striated that an accurate crystallographic study would not be feasible. They possess a distinct bronze lustre which soon disappears owing to superficial decomposition. Upon exposure to the air the substance loses ammonia and iodine, finally leaving cuprous iodide. It is decomposed by water. Heated in aqueous or alcoholic ammonia it dissolves, forming a deep blue solution which upon cooling deposits bright blue needles remaining to be investigated.

From the mother liquors decanted from the black crystals may be obtained by further evaporation at first, $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$, and finally the mixture of $\text{Cu}_8(\text{NH}_3)_{16}\text{I}(\text{C}_2\text{H}_3\text{O}_2)_{15}$, with the coal-black hexagonal crystals already mentioned.† These latter crystals are very different in appearance from $\text{Cu}_3(\text{NH}_3)_{10}\text{I}_6$; they will be investigated in the future.

Analysis of $\text{Cu}_8(\text{NH}_3)_{10}\text{I}_6$.

- I. 0.2049 gram of the substance yielded an amount of ammonia requiring 18.22 cubic centimeters of decinormal acid for neutralization, and 0.0352 gram of copper on electrolysis.
- II. 0.2315 gram of the substance required 20.24 cubic centimeters of acid, and gave 0.0385 gram of copper and 0.2901 gram of argentic iodide.

* Richards and Shaw, *These Proceedings*, XXVIII. 257.

† See page 81.

III. 0.2302 gram of the substance required 20.36 cubic centimeters of acid, and gave 0.2872 gram of argentic iodide.
 IV. 0.2307 gram of the substance required 20.35 cubic centimeters of acid.
 V. 0.2150 gram of the substance on electrolysis gave 0.0367 gram of copper.

No.	Copper.	Ammonia.	Iodine.
I.	17.17	15.19	
II.	16.63	14.94	67.73
III.	—	15.11	67.48
IV.	—	15.07	
V.	17.07		
Averages . .	16.96	15.08	67.61

	Calculated for above Formula.	Found.
Copper	17.00	16.96
Ammonia	15.20	15.08
Iodine	67.80	67.61
	100.00	99.65

(4.) AMMONIC DICUPRIC ACETATE, $\text{NH}_4\text{Cu}_2(\text{C}_2\text{H}_5\text{O}_2)_5 \cdot \text{H}_2\text{O}$.

Since compounds containing three molecules of ammonia, one of acetic acid, and one atom of chlorine, bromine, or iodine had been proved to exist, it became a matter of interest to discover if it were possible to prepare $\text{Cu}(\text{NH}_3)_3(\text{C}_2\text{H}_5\text{O}_2)_2$, in which the halogen is replaced by acetic acid. Many unsuccessful attempts were made to obtain this compound. In the course of these experiments, however, a new double salt of cupric and ammonic acetates was discovered. Four grams of cupric acetate, six grams of glacial acetic acid, and twenty cubic centimeters of alcohol were mixed together, and ammonia gas was passed into the mixture until the green color just turns into blue. The solution became hot from the absorption of the ammonia, and the cupric acetate dissolved readily. After standing a few hours many small bluish green crystals were deposited, which have the com-

position given below. The crystals are soluble in water without decomposition, and are fairly permanent in the air.

Analyses of $\text{Cu}_2\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)_5 \cdot \text{H}_2\text{O}$.

- I. 0.2586 gram of the substance yielded an amount of ammonia requiring 5.49 cubic centimeters of decinormal acid, and an electrolysis gave 0.0717 gram of copper.
- II. 0.4303 gram of the substance required 9.40 cubic centimeters of decinormal acid.
- III. 0.2525 gram of the substance gave 0.0703 gram of copper.
- IV. 0.2604 gram of the substance required 5.52 cubic centimeters of acid, and gave .0725 gram of copper.
- V. 0.3080 gram of the substance gave on combustion 0.2970 gram of carbon dioxide.

No.	Copper.	Ammonium.	Acetic Acid.
I.	27.73	3.84	
II.	—	3.96	
III.	27.86		
IV.	27.84	3.84	
V.	—	—	64.45
Averages . .	27.81	3.88	64.45

	Calculated for above Formula.	Found.
Copper	27.75	27.81
Ammonium	3.94	3.88
Acetic acid	64.38	64.45
Water (by difference)	3.93	3.86
	100.00	100.00

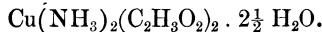
(5 and 6.) CUPRIAMMONIUM ACETATE.

This salt, discovered by Foerster,* may be prepared in an anhydrous condition by allowing an alcoholic solution of cupric acetate containing a slight excess of ammonia to evaporate in the air. Two determina-

* Ber. der deutsch. chem. Gesellsch., 1892, XXV. 3416.

tions of the amount of copper present in the large deep blue crystals showed respectively 29.41 and 29.32 per cent, the theoretical being 29.48. The ammonia was found to be 15.68, instead of the theoretical amount 15.82 per cent, corresponding to the formula $\text{Cu}(\text{NH}_3)_2\text{C}_2\text{H}_3\text{O}_2$.

The crystallized salt containing two and a half molecules of crystal water, also discovered by Foerster, was prepared in blue feathery crystals by the evaporation of aqueous ammoniacal cupric acetate. Analysis showed the percentage of copper present to be 24.23 instead of 24.38, and the ammonia to be 13.02 instead of 13.08 per cent. The theoretical values were calculated for the formula



All of these compounds, as well as many similar ones obtained from other acids and the substituted ammonias, will be further studied at this Laboratory in the near future.